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NUCLEATION OF HELIUM PRECIPITATES IN NICKEL OBSERVED BY HDS

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Thermal Helium Desorption Spectrometry (HDS) has been used to study the room temperature nucleation of helium precipitates at point defects in Ni(110), notably HeV defects at depth ~ 20 nm below the crystal surface. Helium is injected into the crystal by 50 eV He ion-irradiation which causes no atomic displacements. It has been observed that He_nV defects with occupation from $n = 2$ He to $n = 4$ He bind helium equally strongly, but weaker than for HeV. For $n \geq 5$ He the binding increases rapidly. The observed behaviour is attributed to helium induced trap mutation and agrees qualitatively with results of atomistic calculations in nickel for this case. Helium precipitation at near surface trapping sites is held responsible for the observed increase of helium release temperatures with helium dose when an undamaged crystal is irradiated. Preliminary TEM observations of Ni specimens irradiated with 50 times higher helium doses than the maximum dose used in the HDS experiments indicated planar clustering of the helium.

1. INTRODUCTION

The generation of helium in metals exposed to the intense neutron irradiation of fusion reactors has a considerable influence on the development of radiation damage in these metals. Helium binds strongly to vacancies and vacancy complexes and therefore stabilizes the early void nuclei. Though helium initially binds less to other defects, e.g. foreign atoms substituted in the metal matrix^{1,2}, clusters of self-interstitials and most of the dislocations, the binding energy increases gradually with the amount of helium collected by these defects leading to some form of helium precipitates.

Low energy helium injected at room temperature into metal specimens migrates after thermalisation freely towards defects sites deeper in the metal and therefore can be used to follow the nucleation and growth of precipitates in a controlled way. For molybdenum application of this method has led to the discovery with TEM of the platelet morphology of precipitates nucleated at small point defects³ and further has yielded information on platelet growth by

emission of prismatic loops, platelet bubble conversion and helium cracking processes at dislocations^{4,5,6}. Helium desorption measurements provided the information on the early, submicroscopic stages of precipitation. For the bcc metals Mo and W a large number of data has been collected on multiple helium trapping at defects which enabled extrapolation to TEM visible precipitates^{1,7}. THDS experiments on fcc metals are rather scarce. For Ni(100) Kornelsen and Edwards⁸ report on small helium vacancy complexes but no attempt has been made so far to study precipitate growth.

In this paper we report on the results obtained on the growth of helium precipitates at previously prepared HeV defects in Ni(110) by helium filling up to 50 He per precipitate. In section 2 experimental details are described followed by results and discussion in section 3. Conclusions and final remarks are given in section 4.

2. EXPERIMENTAL

The helium desorption spectrometer and the

experimental procedure used in this work is similar to that used in previous precipitation studies of helium in molybdenum^{6,7}. A Ni(110) crystal of purity better than 99.995% has been sputter cleaned and heated many times to 1500K (ramp heating 40 K/s) in UHV. Inherent to the method, the crystal is heated to 1400K every time a desorption spectrum is recorded.

HeV defects are produced by irradiation with 1 keV He-ions (dose $1.5 \times 10^{12} \text{ cm}^{-2}$) followed by ramp annealing to 740K (40 K/s) and cooling down to room temperature. A desorption spectrum taken after this treatment shows a single desorption peak due to HeV dissociation ($\text{HeV} \rightarrow \text{He} + \text{V}$) corresponding with the release of $1.1 \times 10^{11} \text{ He cm}^{-2}$ and thus indicates an identical number of HeV defects. In the helium precipitation experiments the above treatment was repeated but with intermediate 50 eV He-ion irradiation at varying dose before the crystal finally was degassed.

3. RESULTS AND DISCUSSION

3.1. Helium induced "trap-mutation"

Fig.1 shows helium desorption spectra for HeV defects decorated by 50 eV He-ion bombardment with doses varying from 0 to $10^{15} \text{ He cm}^{-2}$. The bottom spectrum shows the H-peak assigned to HeV dissociation. Further helium desorption spectra reveal the occurrence of new peaks denoted M and K. The S-peaks are observed also when an undamaged crystal is irradiated with low energy helium. Therefore, only the G peak and the high temperature peaks should be attributed to the multiple helium filled vacancies (He_nV). The average number of helium $\langle n \rangle$ per defect is obtained by integration of the helium content in G, H, M and K peaks and dividing this number by the initial number of HeV defects.

With regard to the S-peaks Kornelsen and Edwards found for Ni(100) similar low temperature peaks for He-ion irradiation at energies below the threshold energy for atomic displace-

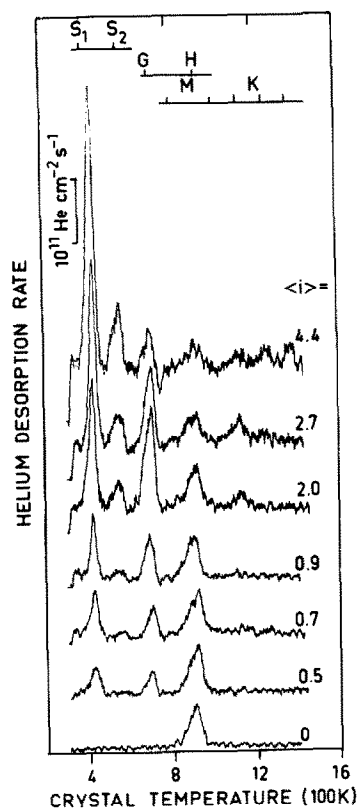


FIGURE 1

Helium desorption spectra for a Ni(110) crystal containing HeV defects which has been irradiated with varying doses of 50 eV He-ions. The average number $\langle i \rangle$ of extra helium trapped per initial HeV defect is indicated. Peaks and series of peaks are indicated by S (surface related) and G, H, M, K (see table 1).

ments by $\text{He}(E_{\text{thresh}} \sim 100\text{eV})$ ⁸. They ascribed these peaks to helium release from surface related sites located within the dynamical range of the He ions at some lattice units of depth below the surface. Further experimental evidence resulting from the present work is reported in section 3.4.

The evolution with dose of the H and G peak is shown in fig.2. On helium filling the H peak remains constant whereas the G peak grows and reaches a maximum helium population. Thereafter the H and G peak both decrease while the total number of helium trapped at the defects increases approximately linearly.

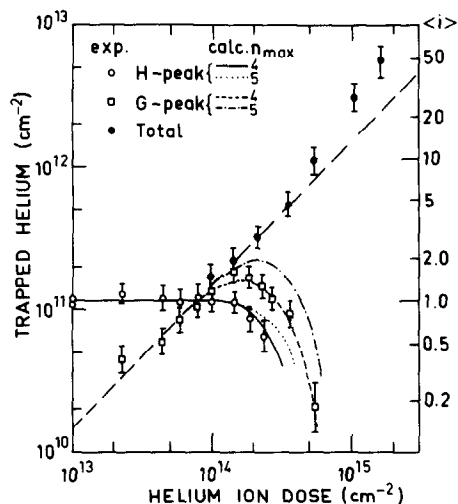


FIGURE 2

Peak population of H- and G-peak, and the total number of trapped helium vs the helium ion dose (ion energy 50 eV). Calculated curves (H,G) are given for $n_{\max}=4$ and $n_{\max}=5$ (see also the text).

Filling theory⁹ applied to the present case, where the helium traps (HeV) are situated much deeper (~ 20 nm average depth is calculated with MARLOWE) than the implantation depth (~ 0.5 nm) of the 50 eV He-ions, gives the number of defects N_i which have trapped i helium as follows:

$$N_i = N_0 (1/i!) (\mu P)^i \exp(-\mu P)$$

where P is the helium dose, N_0 is the initial number of HeV, and μ is a filling constant dependent on the trapping size of the defects and the implantation depth of the helium. The average number of trapped helium per defect $\langle i \rangle = x$. (note that $\langle n \rangle = \langle i \rangle + 1$). The experimental filling curves in fig.2 are matched reasonably well when it is assumed that He_nV defects with $n=2$ to $n=4$ contribute all helium, in excess of one, to the G peak as follows

$$\text{G-peak population} = \sum_{i=1}^3 i N_i$$

and that the H-peak gets contributions only from He_nV with $n < 4$ ($n_{\max}=4$ He).

TABLE 1. Helium release data for He_nV complexes

n	peak/ T in K	release mechanism	$E_{\text{D,He}}^{\text{exp.}}$ (eV)	$E_{\text{B,He}}^{\text{theor.}}$ (eV)		
				He _n V	He _n V ₂	He _n V
1	H 900	HeV → He	2.34 *	2.63 ¹⁰	10	2.82 ¹¹
2	G 720	He ₂ V → He	1.82	1.44		1.81
3	G "	He ₃ V → He	"	1.35		1.70
4	G "	He ₄ V → He	"	1.51		1.95
5	M 750	He ₅ V → He	> 1.8	1.35		1.62
6		MPI-		1.76	1.40	2.20
7		emission.		1.16	2.05	1.37
8		He _n V ₂ → He		1.02	1.63	1.25
9				1.38	2.09	
10	K 950	thermal	> 2.5	1.41	2.04	
"		vacancy				
"		trapping.				
"		He _n V _m → He				

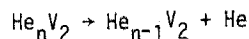
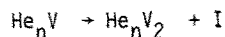
*first order release; a pre-exponential factor $\sim 10^{13} \text{ s}^{-1}$ is assumed; $E_{\text{D,He}}^{\text{exp.}} = E_{\text{B,He}}^{\text{theor.}} + E_{\text{M,He}}$
 $E_{\text{M,He}}$ = helium migration energy

$$\text{H-peak population} = \sum_{i=0}^3 N_i$$

(see calculated curves in fig.2).

In the desorption spectra no peaks associated with He_nV ($n \geq 5$) defects are observed at lower temperature than the G-peak. Instead M-peaks are observed between G and H and around the H peak. Upon average filling of $\langle n \rangle = 4$ He release is observed already at temperatures beyond the H-peak temperature. As in molybdenum we call the onset of this rapid increase of the helium release temperature "trap mutation". Peak assignments and estimates of the dissociation energies involved are given in table 1. The results of atomistic calculations by Wilson et al.¹⁰ and De Hosson et al.¹¹, also given in table 1, predict quite well the trends found for He_nV dissociation from $n=1$ to $n=4$. In particular the nearly equal binding of the 2nd through 4th helium is in agreement with the above peak assignment of the G-peak. The calculations predict lower binding for the 7th through 10th helium than for the 5th helium which is not observed in the experiment. However it might be possible that emission of a mutation produced interstitial

(MPI)¹⁰ occurs before helium is released, e.g. via defect reactions



MPI-binding energies quoted by Wilson et al.¹⁰ decrease from $E^B = 2.25$ eV for $n=7$ to $E^B = 0.3$ eV for $n=10$ which makes the above process likely to occur at ~ 9 or 10 He. The helium binding after MPI emission amounts to ~ 2 eV and explains the experimental increase of He release tem-

perature. A discrepancy exists where the release of the 5th through 8th He is concerned. A similar discrepancy found for trap mutation in Mo is discussed in refs.7 and 12.

3.2. Growth to larger precipitates ($n > 10$)

In fig.3 results are shown of further helium filling of the HeV defects. It appears that the release temperature of the helium attached to the He_nV defects increases rapidly with dose; at $\langle i \rangle = 50$ He per defect the temperature has increased to 1400K ($0.8 T_m$). It should be remarked that trapping of thermally generated vacancies during heating plays a role in the helium release process. Assuming $(E_V^F + E_V^M) = 2.5$ eV more than one vacancy is calculated to be trapped per defect at 950K. Thus beyond this temperature the precipitates will firstly convert to equilibrium bubbles before dissociation or bubble diffusion takes place. Therefore no comparison can be made with calculated helium binding energies of helium precipitates of this size ($n > 10$).

3.3. Surface related precipitation

The earlier assignment of S-peaks to release from surface related helium traps was given support by experiments which involved low energy (50 eV) Ar-ion irradiation of the crystal. A dose of 10^{14} Ar-ions cm^{-2} was sufficient for complete removal of the S-peaks, whereas at doses as high as 10^{15} cm^{-2} only partly removal of the HeV defects was observed. Apparently the dynamical interaction of the argon projectiles or nickel recoil atoms with the shallow implanted helium caused its release. The deeper situated HeV defects were affected only by the interaction of irradiation produced self-interstitials which migrated to deeper layers and caused release via the recombination reaction $\text{HeV} + \text{I} \rightarrow \text{He}$.

Though the evolution with dose of the surface peaks in fig.3 complicates the evaluation of precipitate growth at bulk defects it might indicate how precipitates grow in the absence of vacancies. It is observed that trapping of

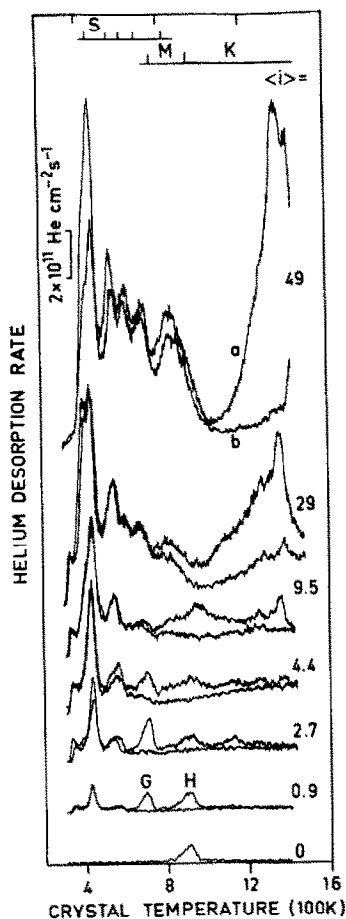


FIGURE 3

Helium desorption spectra for Ni(110) irradiated with varying dose ($0 - 1.65 \times 10^{15} \text{ cm}^{-2}$) 50 eV He-ions. The two spectra plotted for every dose number correspond with a) a crystal containing previously prepared HeV defects and b) without these defects. The average number $\langle i \rangle$ of helium trapped per HeV defect is indicated.

helium in shallow traps leads by increased filling to helium apparently in deeper traps (fig. 3 top spectrum). A scheme for precipitation of interstitial helium given by Wilson et al.¹⁰ might be applicable for this case. These authors quote a binding energy of ~ 1 eV for He_5 precipitate and a MPI binding energy of .61 eV which make it likely that MPI emission occurs at room temperature or slightly beyond. The He_5V defect thus created binds helium stronger than the He_5 defect.

3.4. TEM RESULTS

TEM observation of Ni(110) specimens that were irradiated up to doses of 10^{17} He/cm², 50 eV He, revealed a variety of images with sizes of the order of 10 nm. In some cases the images showed similar appearance as the platelets found in molybdenum^{3,6}. However, also groups of small bubbles lying on {111} planes could be identified.

The number of helium atoms trapped per defect cannot be extrapolated well from the present HDS results, because the helium filling $\langle i \rangle$ has been measured only to ~ 50 He/trap (fig.2). Furthermore the continued growth of surface related precipitates might have caused a reduction in the flow of helium to the interior of the crystal.

4. CONCLUSIONS

The HDS results obtained for helium precipitation at mono-vacancies in nickel reveal:

1. The occurrence of "trap mutation" of He_nV at $n \sim 5$ He.
 2. High thermal stability of relatively small helium vacancy clusters (20-50 He).
 3. Qualitative agreement with results of atomistic calculations. A discrepancy exist for the binding of the 5th through 8th helium atom.
- In addition, evidence is found for considerable growth of precipitates near the Ni(110) surface.

Future work will be aimed to circumvent the problem of near-surface helium precipitation. Helium injection at elevated temperatures e.g.

500 K probably will prevent the growth of these precipitates so that a constant flow of helium to deeper defects is guaranteed.

The near-surface zone 'damaged' by the above precipitation may have some similarity with the helium rich surfaces created when blisters have formed on nickel surfaces. Helium desorption spectra taken beyond the critical dose for blistering¹³ show low temperature desorption (~ 450 K) similar to the S_1 peak in this work.

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